Hydrogen Abstraction from Silylamines; an Investigation of the 1,2-Migration of the Trimethylsilyl Group in Aminyl Radicals

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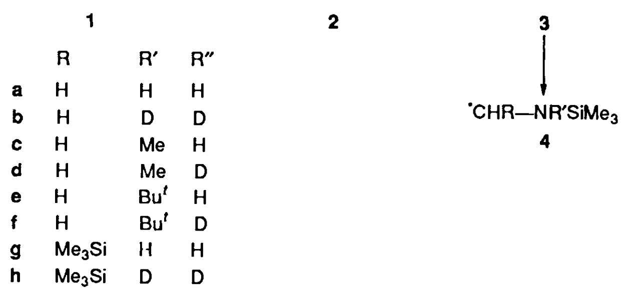
Hydrogen abstraction from a series of silyl-substituted amines, $Me_3SiCHRNHR'$, by *tert*-butoxyl radicals has been examined by EPR spectroscopy. For each amine hydrogen is abstracted from both the methylene (or methine) group and from the amino group to give a mixture of aminoalkyl, $Me_3SiC^{\bullet}RNHR'$, and aminyl radicals, $Me_3SiCHRN^{\bullet}R'$. The proportion of hydrogen abstraction from the amino groups is less than from the methylene (methine) groups. The aminyl radicals are not directly detectable by EPR spectroscopy, but they rearrange above a particular temperature by 1,2-migration of the trimethylsilyl group from carbon to nitrogen to give carbon-centred radicals, $^{\bullet}CHRNR'SiMe_3$, which have been spectroscopically characterised. Mechanistic evidence favours an intramolecular migration of the trimethylsilyl group *via* a transition state in which the silicon atom expands its valence shell to five, rather than *via* an elimination–readdition route. Rate parameters for the migrations have been estimated from the temperature development of the rearranged radical concentrations and found to be sensitive to the presence of sterically large groups at the nitrogen terminus.

The disinclination of alkyl (but not aryl) groups to undergo 1,2-migration reactions in free radicals is well known.[1] Usually a migrating group must possess a vacant, low lying orbital, in which the unpaired electron can be accommodated during the transfer, in order to lower the activation barrier enough to permit this rearrangement. Silicon is the next element below carbon in the second row of the periodic table but for silyl group migrations the vacant d-orbitals on silicon are probably too high in energy[2] to stabilise the transition state of a 1,2-migration. However, silicon easily expands its valence shell to become five-coordinate, and this may explain the fact that a few 1,2-migrations of the trimethylsilyl group have been observed under normal solution phase conditions. Although no examples of the 1,2-migration of R_3Si groups from carbon to carbon are known,[3–5] migration of the Me_3Si group from silicon to carbon has been observed in the gas phase,[6,7] but not in solution.[8] 1,2-Migrations of silyl groups from silicon to sulfur[9] and from oxygen to nitrogen[10] have also been reported. We reasoned that because the Si–N and Si–O bond strengths are much higher than the Si–C bond strength,[11] this inbuilt thermodynamic bias would encourage 1,2-migrations from carbon to nitrogen in aminyl radicals (Scheme 1), and from carbon to oxygen in oxyl radicals.

In a preliminary communication we reported that migration of the Me_3Si group from carbon to nitrogen in the $Me_3SiCH_2NH^{\bullet}$ radical (**3a**) could be observed by EPR spectroscopy, as could an analogous migration from carbon to oxygen in the $Me_3SiCH_2O^{\bullet}$ radical.[12]



	R	R′	R″
a	H	H	H
b	H	D	D
c	H	Me	H
d	H	Me	D
e	H	Bu^t	H
f	H	Bu^t	D
g	Me$_3$Si	H	H
h	Me$_3$Si	D	D

Scheme 1

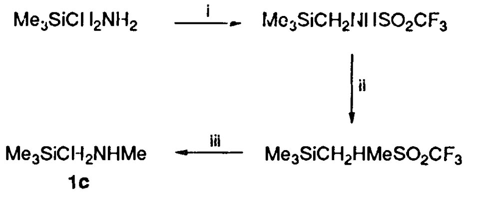
tert-Butoxyl radicals abstract hydrogen in primary amines *both* from the carbon atom adjacent to nitrogen, and from the amino group itself, to give a mixture of aminoalkyl and alkylaminyl radicals[13] [eqn. (1)]. Primary alkylaminyl radicals

$$R_2CHNH_2 + Bu^tO^{\bullet} \longrightarrow R_2C^{\bullet}NH_2 + R_2CHNH^{\bullet} + Bu^tOH \quad (1)$$

produced in this way cannot be detected by EPR spectroscopy in solution, although secondary aminyl radicals can; the reason for this remains obscure.[14] Rather few silyl-substituted amines are known, and their reactions with free radicals have only been explored in a very nominal way. We have now prepared a range of silylamines (**1**) and studied hydrogen abstraction from them; we report in this paper a spectroscopic examination of the silyl-substituted radicals so formed, and their rearrangements.

Results and Discussion

Preparation of the Silylamines.—Trimethylsilylmethylamine (**1a**) was originally made by a Gabriel synthesis on (chloromethyl)trimethylsilane. *N*-Methyltrimethylsilylmethylamine (**1c**) was prepared by methylation of *N*-trimethylsilylmethyltriflamide with methyl iodide and potassium carbonate. The amine **1c** was released by reduction of the methyltriflamide with lithium aluminium hydride (Scheme 2). This amine was purified by conversion to the hydrochloride and subsequent release of the amine by potassium hydroxide, followed by preparative gas



Scheme 2 *Reagents and conditions:* i, $(CF_3SO_2)_2O$–CH_2Cl_2, 0 °C; ii, MeI–K_2CO_3–Me_2CO, iii, $LiAlH_4$–Et_2O

Table 1 EPR parameters of radicals derived from silylamines[a]

Radical	T/K	hfs/mT				
$Me_3SiCH^{\bullet}NH_2$ (**2a**)	220	1.60 (1 H_α)	0.63 (1 N)	0.072 (1 NH_2)	0.036 (1 NH_2)	0.036 (9 H)
$Me_3SiCH^{\bullet}ND_2$ (**2b**)	260	1.57 (1 H_α)	0.62 (1 N)			0.035 (9 H)
$Me_3SiCH^{\bullet}NHMe$ (**2c**)	240	1.60 (1 H_α)	0.63 (1 N)			0.03 (9 H)
$Me_3SiCH^{\bullet}NHBu^t$ (**2e**)	225	1.50 (1 H_α)	0.72 (1 N)	0.25 (1 H)		0.034 (9 H)
$(Me_3Si)_2C^{\bullet}NH_2$ (**2g**)	220		0.63 (1 N)	0.28 (1 H)	0.28 (1 H)	0.03 (18 H)
$(Me_3Si)_2C^{\bullet}ND_2$ (**2h**)	280		0.64 (1 N)	0.03 (1 D)	0.03 (1 D)	0.03 (18 H)
$Me_3SiNHCH_2^{\bullet}$ (**4a**)	260	1.63 (2 H)	0.24 (1 N)	0.24 (1 H)		
$Me_3SiNDCH_2^{\bullet}$ (**4b**)	260	1.60 (2 H)	0.24 (1 N)	0.040 (1 D)		
$Me_3SiN(Bu^t)CH_2^{\bullet}$ (**4e**)	300	1.48 (2 H)	0.37 (1 N)			
$Me_3SiCH^{\bullet}NHSiMe_3$ (**4g**)	280	1.44 (1 H)	0.45 (1 N)	0.18 (1 H)	0.03 (9 H)	
$Me_3SiCH^{\bullet}NDSiMe_3$ (**4h**)	280	1.44 (1 H)	0.45 (1 N)	0.03 (1 D)	0.03 (9 H)	

[a] All g-factors 2.003 ± 0.001.

chromatography. The *N*-tert-butyltrimethylsilylmethylamine (**1e**) was made by direct alkylation of *tert*-butylamine with iodomethyltrimethylsilane. Bis(trimethylsilyl)methylamine (**1g**) was made from trimethylcyanosilane through reductive silylation using lithium as the reducing agent, trimethylchlorosilane as the electrophile and an HMPA/THF mixture as the solvent. The deuteriated amines were obtained by shaking each amine with excess deuterium oxide for *ca.* 10 min.

Hydrogen Abstraction from the Silylamines.—The amine **1a** and di-*tert*-butyl peroxide in cyclopropane solvent (150–200 K) or *tert*-butylbenzene solvent (200–370 K) were photolysed in the cavity of an EPR spectrometer. In the temperature range 150–230 K a single radical, readily identified as the aminotrimethylsilylmethyl radical (**2a**), was observed (EPR parameters in Table 1). This spectrum underwent a complex series of changes as temperature was increased, due to changes in the magnitudes of the amino hydrogen hyperfine splittings (hfs). Selective line broadening due to restricted rotation about the $H_2N–C^{\bullet}$ bond was observed above 320 K, with coalescence at about 370 K; boiling was too serious about this temperature for the fast exchange limit to be spectroscopically delineated. For a simple two-jump process such as this the rate constant for rotation about the $H_2N–C^{\bullet}$ bond, at coalescence, is given by eqn. (2),[15] where a_1 and a_2 are the hfs in Gauss (1 mT = 10 G)

$$k/s^{-1} = 6.22 \times 10^6 (a_1 - a_2) \qquad (2)$$

of the two amino hydrogens in the slow exchange limit. Since $a_1 - a_2 = 0.05$ mT we obtain k (370 K) = 3.1×10^6 s^{-1}. The Arrhenius pre-exponential factors for bond rotations of this type are usually[16] 10^{13} s^{-1} and, assuming that this holds true here, leads to a value of 11.3 kcal mol^{-1} for the Arrhenius activation barrier.

Above 230 K a second radical appeared reaching full intensity at 260 K (EPR hfs in Table 1). As described previously[12] this is the aminoalkyl radical **4a** formed by a 1,2-silyl migration in the aminyl radical **3a**. Because **3a** is a primary alkylaminyl radical it is EPR 'silent' (see above)[14] but, when its rearrangement becomes sufficiently rapid at *ca.* 230 K, the rearranged radical **4a** appears in the spectrum. These conclusions were confirmed by spectroscopic examination of the deuteriated amine **1b** which afforded the *N*-deuterio radical **4b** at $T > 230$ K.

Hydrogen abstraction from the substituted silylamines **1c–h** was next investigated. The EPR spectra obtained on photolysis of the *N*-methyl amines **1c** and **1d** with di-*tert*-butyl peroxide were extremely weak and complex. The major radical detected had a(1 H) = 1.60 and a(N) = 0.63 mT, together with several smaller hfs. By analogy with **2a** we attribute this spectrum to **2c** (Table 1). At $T = 260$ K the spectrum showed evidence of another radical, so that the expected 1,2-silyl migration probably occurs, but the weakness and complexity of the spectra prevented definitive analysis. It is possible that the secondary aminyl radical **3c** contributed to the complex pattern.

Hydrogen abstraction from the *N*-*tert*-butylamine **1e** gave rise to a well resolved spectrum of a single radical at 220 K [Fig. 1(*a*)]. The hfs are similar to those of other silylaminomethyl radicals and we attribute this spectrum to **2e** (see Table 1). This spectrum changed little on increasing the temperature, apart from a general increase in the line width. However, at about 300 K the spectrum of a second, minor radical, began to appear and reached its fullest intensity at *ca.* 360 K [Fig. 1(*b*)]. This minor radical showed hfs from two equivalent hydrogen atoms and a nitrogen atom (see Table 1) and corresponded to the rearranged radical **4e**, formed by a 1,2-silyl migration in **3e**. At 360 K the concentration ratio [**2e**]/[**4e**] was found to be 11.5. This very high ratio is an indication that the bulky *tert*-butyl group inhibits hydrogen abstraction from the amino group of **2e** so that the concentrations of the aminyl radical **3e**, and its rearrangement product **4e**, are low in the accessible temperature range. The spectral intensity of the secondary aminyl **3e** would be divided amongst many lines and, because its proportion is so low, this probably explains why it could not be detected. The rearranged radical also makes its appearance at a higher temperature than for **3a**. It is likely that this is a consequence of the presence of the large *tert*-butyl group at the *N*-terminus of the rearrangement which slows down the silyl migration. On prolonged photolysis additional spectra due to degradation products began to show up.

The only detectable radical on hydrogen abstraction from the bis(trimethylsilyl)methylamine **1g** at $T < 220$ K was the carbon-centred species **2g** (EPR parameters in Table 1). This spectrum dominated in the temperature range 220–345 K and was distinguished by a steady decrease in the hfs of the two amino hydrogens from 0.28 to 0.18 mT. These two hydrogen atoms remained equivalent in this temperature range and no exchange broadening was observed. At *ca.* 220 K the spectrum of a second minor radical appeared and reached its full intensity at 250 K. The lines from this minor radical were badly overlapped by the main spectrum and consequently it was difficult to analyse. However, in the case of the deuterium-substituted amine **1h**, the spectral spread of the multiplets from **2h** was less and a satisfactory simulation of **4h** was achieved (Fig. 2). The minor amount of **4h** as compared to **2h** ([**2h**]/[**4h**] = 9 at 280 K) indicated that hydrogen abstraction from the methine group was much faster than from the amino group.

For all the amines studied the [**2**]/[**4**] ratio was large and hence hydrogen abstraction by *tert*-butoxyl radicals was faster from the methylene, or methine, groups of the silylamines than

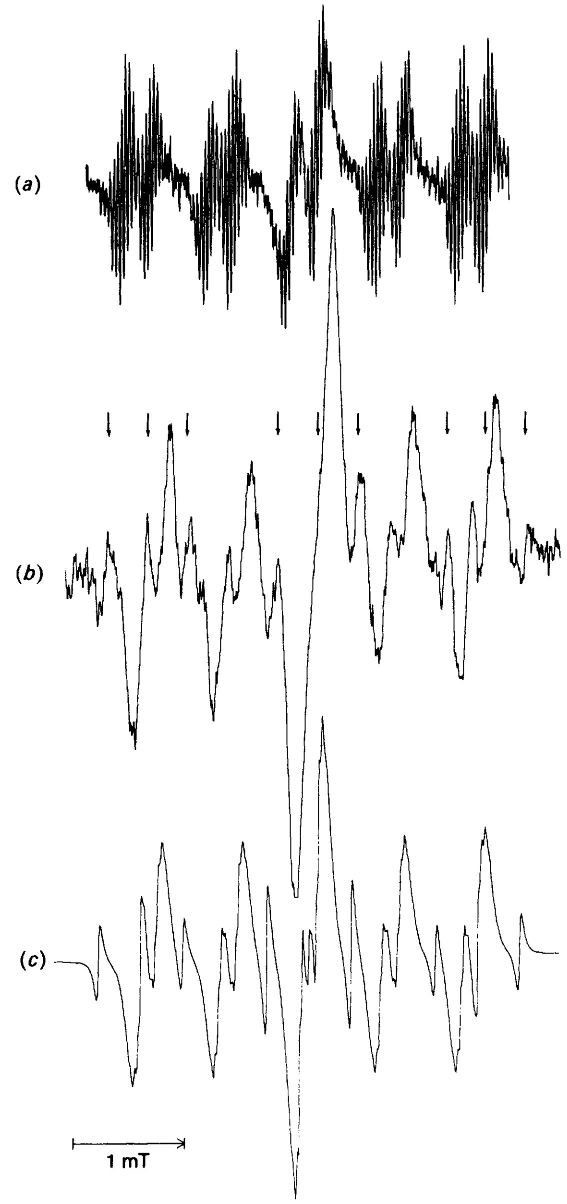


Fig. 1 9.3 GHz EPR spectra derived from *N-tert*-butyltrimethylsilylmethylamine (**1e**) in *tert*-butylbenzene. (*a*) Spectrum of radical **2e** at 220 K. (*b*) Spectrum at 360 K showing a mixture of radical **2e** with broader lines; rearranged radical **4e** denoted with arrows. (*c*) Computer simulation including both radicals.

from the amino groups even when the amino hydrogens were more sterically exposed, as for example in **1a**. Several factors may contribute to this. First, because the electronegativity difference between oxygen and carbon is greater than that between oxygen and nitrogen, hydrogen abstraction from carbon by the electronegative *tert*-butoxyl radical will be favoured by a polar effect. Second, the trimethylsilyl group is known to be an electron attractor in free radical reactions,[17] hence the radical produced by abstraction from the carbon atom *i.e.* **2** contains both electron releasing and electron attracting groups at the radical centre and therefore may have weak capto-dative stabilisation.

The barrier to rotation about the $H_2N\text{–}C^{\bullet}$ bond in **2a** (see above) is a measure of the stabilisation energy of this radical.[16,18,19] It is noteworthy that the rotation barrier in **2a** is nearly 4 kcal mol^{-1} higher than the analogous rotation barrier in the radical obtained by replacing the silicon atom of **2a** by a carbon atom ($Me_3CCH^{\bullet}NH_2$) for which the $H_2N\text{–}C^{\bullet}$ bond

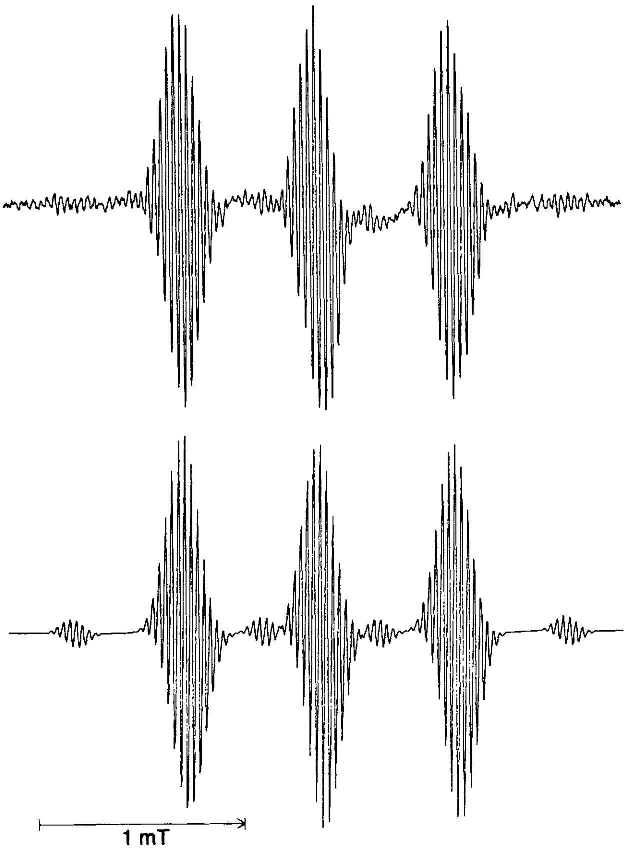
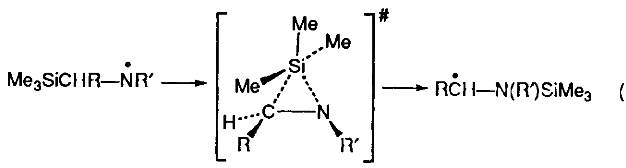


Fig. 2 Top: 9.3 GHz EPR spectrum derived from deuteriated bis(trimethylsilyl)methylamine at 280 K and showing radicals **2h** and **4h**. Bottom: computer simulation including both radicals.

rotation barrier is[16] 7.5 kcal mol^{-1}. This result is consistent with a higher stabilisation energy for the C–D radical **2a**, although other explanations are possible.

1,2-*Silyl Migrations in Aminyl Radicals*.—The migration of the Me_3Si group from carbon to nitrogen could occur intramolecularly *via* a transition state (**5**) in which the silicon atom expands its valence shell to five [eqn. (3)]. Alternatively, the



(3)

5

rearrangement could take place by β-elimination of a trimethylsilyl radical and formation of an imine, which subsequently recaptures the trimethylsilyl radical by addition at the nitrogen terminus [eqn. (4)].

$$Me_3SiCHR\text{-}N^{\bullet}R' \longrightarrow Me_3Si^{\bullet} + RCH{=}NR' \longrightarrow RCH^{\bullet}\text{-}N(R')SiMe_3 \quad (4)$$

The main products derived from these reactions consisted of polymer together with oxidised derivatives of trimethylsilane.[12] These products shed little light on the mechanism of the rearrangement because they could be derived by oxidation or polymerisation of primary products in either case.

In the elimination–addition mechanism [eqn. (4)] a trimethylsilyl radical is released into the medium. We attempted therefore to distinguish between the two routes by trapping this

Table 2 Estimated kinetic parameters for 1,2-migration of the trimethylsilyl group from carbon to nitrogen in aminyl radicals

Migration in:	$T(=)$/K	E/ kcal mol^{-1}	log[A/s^{-1}]^a	k/s^{-1} (300 K)
$Me_3SiCH_2NH^\bullet$ (**3a**)	245	11.0	11.5	3×10^3
$Me_3SiCH_2N^\bullet Bu^t$ (**3e**)	310	13.8	11.5	3×10^1
$(Me_3Si)_2CHNH^\bullet$ (**3g**)	235	10.5	11.5	7×10^3

^{a} Assumed values.

species. Organosilyl radicals are good halogen abstractors, but when 2-chloro-2-methylpropane was added to the reaction mixture containing **1e**, no *tert*-butyl radicals were detected by EPR spectroscopy, *i.e.* reaction (5) was not appreciable. 1,3,5-Trinitrobenzene is known to be a good spin trap for trimethylsilyl radicals.[20] However, when this trap was added to the reaction mixture containing **2e**, the spin adduct of the trimethylsilyl radical was not detected. Although this evidence does not allow us to completely dispose of route (4) it suffices to show that the intramolecular process (3) is the most probable.

$$Me_3Si^\bullet + Me_3CCl \longrightarrow Me_3SiCl + Me_3C^\bullet \qquad (5)$$

For the series of amines **1a–h** the onset of each silyl migration was marked by the appearance of the corresponding rearranged radical **4** in the EPR spectra. Because the unrearranged aminyl radicals **3** were not detectable, the rates of the 1,2-migrations could not be measured by the usual kinetic EPR method. However, we estimated the rearrangement dynamics in the following way. The temperatures, $T(=)$, at which the rearranged radicals **4** reached half their final concentration were approximated from the temperature development of the EPR spectra (see Table 2). $T(=)$ will represent the midpoint of each rearrangement where the unrearranged and rearranged radicals are equal in concentration. In general this midpoint depends on instrumental factors such as the irradiation intensity and spectrometer sensitivity, as well as the rates of initiation, termination and rearrangement. We have shown that for a wide range of unimolecular rearrangements studied on the St. Andrews spectrometer there exists a linear correlation between $T(=)$ values and the Arrhenius activation energies.[21] The kinetic parameters of the 1,2-silyl migrations were roughly estimated by making use of this correlation and are noted in Table 2. In each case an Arrhenius pre-exponential factor of the same magnitude as that found for previously studied 1,2-migrations[1,22] was assumed. The rate parameters in Table 2 show that silyl migration is sensitive to steric effects because the rate constant for radical **3e**, which contains a bulky *tert*-butyl group at the nitrogen terminus, is very much smaller. The rate constant for **3g**, with two trimethylsilyl groups available for migration, is greater than that for **3a** by approximately the statistical amount. Kinetic data from other 1,2-migrations with which to compare these results is rather limited and mostly confined to unsaturated carbon-centred groups migrating from carbon to carbon. For these processes rate constants in the range from 1 s^{-1} to 10^7 s^{-1} at 298 K have been obtained.[22]

Experimental

EPR spectra were recorded with a Bruker ER 200D spectrometer operating at 9.3 GHz with 100 kHz modulation. Solutions were prepared in Spectrosil quartz tubes, degassed by bubbling nitrogen for 10 min, or by several freeze–pump–thaw cycles, and irradiated in the spectrometer cavity by light from a 500 W super pressure mercury lamp. Matching of experimental and computer simulated spectra was carried out as described previously.[12]

Trimethylsilylmethylamine.—This compound was prepared by a Gabriel synthesis from (chloromethyl)trimethylsilane,[23] and also obtained commercially.

N-*Trimethylsilylmethyl*-N-*methyltriflamide.*[24]—Methyl iodide (1.95 g, 13.7 mmol) was added to a stirred solution of *N*-trimethylsilylmethyltriflamide[24] (3.17 g, 13.5 mmol) and anhydrous K_2CO_3 (1.89 g, 13.7 mmol) in acetone (150 cm^3). The solution was stirred for 19 h, the acetone was evaporated and the white residue was extracted with chloroform. The combined organic extracts were washed with water, dried ($MgSO_4$), and evaporated to give the title amide as a yellow oil (3.1 g, 92%); δ_H 0.15 (9 H, s), 2.9 (2 H, s), 3.1 (3 H, s).

N-*Methyltrimethylsilylmethylamine.*—*N*-Trimethylsilylmethyl-*N*-methyltriflamide (1.28 g, 5.1 mmol) in anhydrous ether (10 cm^3) was added to a stirred suspension of $LiAlH_4$ (0.59 g, 15.6 mmol) in anhydrous ether (40 cm^3). The mixture was refluxed for 24 h, cooled, and the excess $LiAlH_4$ was decomposed by dropwise addition of water (10 cm^3). The solution was filtered, the ether layer was separated, dried ($MgSO_4$) and distilled to give the amine (0.22 g, 15%), b.p. 96 °C/760 Torr, contaminated with a minor amount of ether. The compound was purified by passing HCl gas through an ether solution of the amine, collecting the immiscible oil which separated and pumping off the ether at high vacuum. The amine was generated by adding crushed KOH to the hydrochloride and collecting it in a cold finger on a vacuum line. Some samples were also purified by preparative GLC using a 3 m column packed with 2% KOH and 10% Carbowax 20M on Chromosorb WAW at 80 °C; δ_H 0.06 (9 H, s), 1.41 (1 H, bs), 2.07 (2 H, s), 2.50 (3 H, s); δ_C −2.55, 41.40, 43.24.

N-tert-*Butyltrimethylsilylmethylamine.*—*tert*-Butylamine (1.2 g, 17 mmol), iodomethyltrimethylsilane (3.6 g, 17 mmol) and triethylamine (1.7 g, 17 mmol) were heated in a sealed tube at 80 °C for 48 h. The product was filtered and chromatographed over silica (diethyl ether/methanol) to give the title compound (0.9 g, 33%). The amine was purified by preparative GLC on the same column described above at 40 °C; δ_H 0.03 (9 H, s), 1.06 (9 H, s), 1.97 (2 H, s); δ_C −2.63, 28.40, 31.45, 51.12.

[Bis(trimethylsilyl)methyl]amine, 'BSMA'.[25]—A mixture of HMPA (180 cm^3, 1 mol) and dry THF (50 cm^3) was added dropwise to a well stirred mixture of trimethylchlorosilane (504 cm^3, 4 mol), lithium (5.6 g, 0.8 mol) and trimethylsilylcyanide (9.9 g, 0.1 mol)[26] so that the temperature remained between 0 and 5 °C. The lavender coloured mixture obtained after 10 h stirring was evaporated to remove THF and excess trimethylchlorosilane. The residue was extracted with pentane (4 × 50 cm^3) and the extract washed with water, neutralised, dried over Na_2SO_4 and evaporated to give a yellow oil. To this oil and methanol (20 cm^3, 0.05 mol) at 0 °C was added trimethylchlorosilane (15 cm^3, 0.05 mol) dropwise with stirring. The mixture was stirred at room temperature for 15 min and evaporated under reduced pressure to afford the white hydrochloride of BSMA in quantitative yield. The hydrochloride was dissolved in ice–water (10 cm^3, 0.05 mol) and a 20% sodium hydroxide solution was slowly added. The mixture was extracted with diethyl ether (4 × 20 cm^3) and the extract was washed with brine, dried over NaOH and distilled to give BSMA (98%), b.p. 70 °C/25 Torr. For preparative purposes, protolysis performed directly on the crude product of the reductive silylation reaction, followed by neutralisation of the salt, afforded BSMA in 65% overall yields. ν/cm^{-1} 3300 (NH_2); δ_H 0.01 (18 H, s, $SiMe_3$), 1.56 (1 H, s, CH), 1.0 (2 H, s, D_2O exch., NH_2); δ_C −1.8 ($SiMe_3$), 31.4 (CH); δ_{Si} 2.11 [9 H,

^2J(H–Si) 6.34] [1 H, ^2J(H–Si) 8.34]; *m*/*z* (%) 175 (1.9), 160 (14.6), 102 (84.9), 74 (100) (Calc. for $C_7H_{21}NSi_2$: C, 47.93; H, 12.07; N, 7.98; Si, 32.02. Found: C, 47.85; H, 11.85; N, 7.4; Si, 30.5%).

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